

# The Stability of the Carbon-Sulfur Bond in Some Aliphatic Sulfonic Acids

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## A DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE  
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH  
REQUIREMENTS FOR THE DEGREE OF  
DOCTOR OF PHILOSOPHY

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By

FREDERICK CARVER WAGNER

Baltimore, 1929

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EASTON, PA.:

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The author wishes to take this opportunity to express his gratitude to Professor E. Emmet Reid for suggestions and inspiration received from him in conference and in the laboratory. He desires also, to record here his thanks to Professors Frazer and Patrick, Associate Professor Rice and Doctors Andrews, Urey and Thornton for invaluable instruction and guidance in the work pursued in the University.

## THE STABILITY OF THE CARBON-SULFUR BOND IN SOME ALIPHATIC SULFONIC ACIDS

Frequent reference is found in the literature to the preparation and some of the properties of aliphatic sulfonic acids but, with the exception of the study by Spring and Winnsinger<sup>1</sup> of the effect of the sulfonic acid group ( $-\text{SO}_3\text{H}$ ) on the chlorination of the alkyl residue, no one reaction has been applied to a series of these acids to observe the effect of change of structure on the chemical reactivity.

The stability of the carbon-sulfur bond in a series of mercaptans has recently been investigated.<sup>2</sup> It seemed of interest to study the sulfonic acids in comparison with the mercaptans.

### Discussion of Results

The normal alkyl sulfonic acids from methyl to hexyl and the secondary from isopropyl to *sec.*-hexyl and also benzene and benzyl sulfonic acids have been prepared and their sodium salts heated in excess of sodium hydroxide solution at temperatures from 315 to 375°.

The percentages of the sulfonic acids decomposed in three hours at 345° are plotted in Fig. 1. Methyl sulfonic acid is remarkably stable while ethyl is decomposed much more rapidly than the other primary acids. From ethyl on, the decomposition decreases as the carbon chain lengthens, both in the primary and in the secondary series. The secondary sulfonic acids are decomposed much more rapidly than the corresponding primary acids. The percentages of the sulfonic acids decomposed are plotted against the temperatures in Fig. 2. These are the same relations

<sup>1</sup> Spring and Winnsinger, *Ber.*, **16**, 327 (1883); **17**, 537 (1884).

<sup>2</sup> Billheimer and Reid, *J. Am. Chem. Soc.*, **52**, 4338 (1930).

that were found with the mercaptans. However, the sulfonic acids are much more stable than the mercaptans; *n*-butyl sulfonic acid requires three hours' heating with 1.85 *N* caustic soda at 365° for 50% decomposition

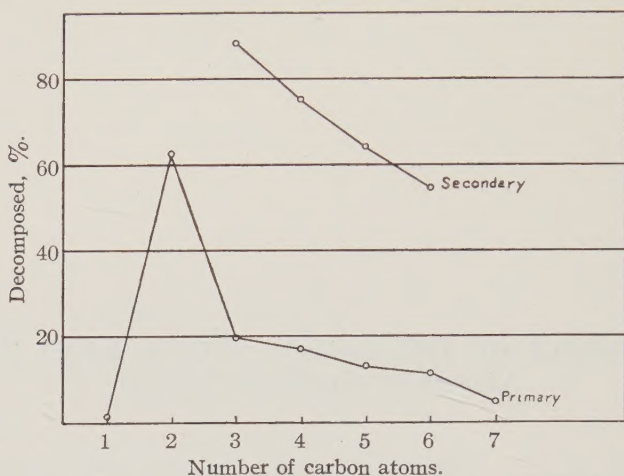


Fig. 1.—Decomposition of aliphatic sulfonic acids with 3.70 *N* NaOH for 3 hours at 345°.

sition, while the same percentage of decomposition of *n*-butyl mercaptan could be effected with the same strength of alkali and in the same time at approximately 100° lower temperature. Assuming the usual tempera-

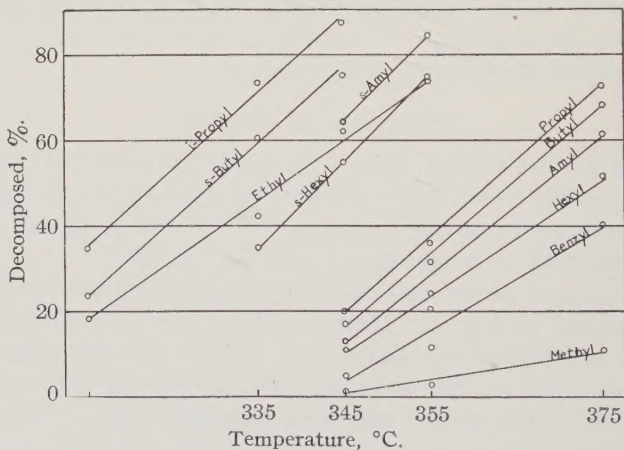
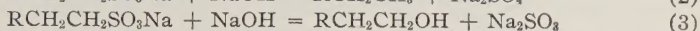
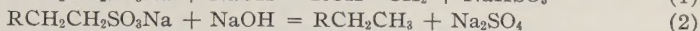
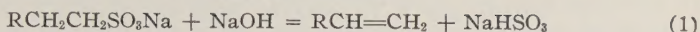


Fig. 2.

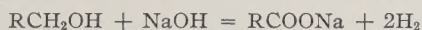
ture coefficient, this means that under the same conditions the carbon-sulfur bond in the mercaptans is broken something like a thousand times as rapidly as in the sulfonic acids.



There are obviously three possible reactions



The experimental work shows that sodium sulfite, with only traces of sulfate, is formed. Berthelot reported reaction (1) as the primary reaction on fusing the potassium salts with potash. In view of this, in several of the runs the residual gas left in the bomb after the slight pressure had been released was swept out by nitrogen and bubbled through dilute bromine water. No appreciable decolorization occurred at any time. Thus, qualitatively at least, reaction (1) is eliminated and reaction (3) remains as the most probable. In one experiment an unsuccessful attempt was made to isolate the alcohol as the half-ester of phthalic acid but none could be separated. It is possible that a small amount of the alcohol could escape detection but it is much more probable that the alcohol had reacted with the alkali at the high temperature of the experiments to form the corresponding acid.



The solutions resulting from the decomposition of *n*-butyl and *n*-amyl sulfonic acids were, in several cases, acidified and gave distinct odors of butyric and valeric acids. Hence it may be concluded that the decomposition is according to reaction (3).

That the chief reaction is a simple one was further adduced by calculation of the velocity constants at the various temperatures by use of the usual expression for second order reactions. The validity of this expression was checked by varying the times of several runs both in the case of *n*-butyl and of *n*-amyl sulfonic acid. The good agreement of the values for  $K_{355}$  for one hour ( $11.76 \times 10^{-4}$ ) and  $K_{335}$  for three hours ( $11.75 \times 10^{-4}$ ) for *n*-butyl and for  $K_{335}$  for one and one-half hours ( $33.5 \times 10^{-4}$ ) and  $K_{335}$  for three hours ( $32.0 \times 10^{-4}$ ) for *n*-amyl justify the use of this expression.

In addition the fractional life found was used to check back against the times measured and again good agreement was found.

By use of the velocity constants and the integrated form of the Arrhenius equation, values of  $Q$ , Table I, were calculated. As can be seen, these values vary slightly in degree but not in order of magnitude.

### Experimental

Some of the sulfonic acids were prepared by Hemilian's<sup>3</sup> modification of Strecker's synthesis<sup>4</sup> while the others were made by oxidation of the mercaptans to the corresponding sulfonic acids by concentrated nitric

<sup>3</sup> Hemilian, *Ann.*, **168**, 146 (1873).

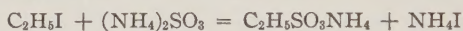
<sup>4</sup> Strecker, *ibid.*, **148**, 92 (1868).

TABLE I  
VALUES FOR  $K$  CALCULATED FROM THE FORMULA

$$K = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad t = 180 \text{ min.}$$

| All values of $K$ multiplied by $10^4$ |           |           |           |           |           |                   |        |
|----------------------------------------|-----------|-----------|-----------|-----------|-----------|-------------------|--------|
| Sulfonate                              | $K_{315}$ | $K_{326}$ | $K_{345}$ | $K_{355}$ | $K_{373}$ | $K_{355}/K_{345}$ | $Q$    |
| Methyl                                 |           |           | 0.440     | 0.988     | 3.558     | 2.24              | 54,700 |
| Ethyl                                  | 6.43      | 19.3      | 32.4      | 46.1      |           | 1.42              | 36,000 |
| Propyl                                 |           |           | 7.21      | 14.12     | 45.13     | 1.96              | 48,600 |
| Butyl                                  |           |           | 5.55      | 11.75     | 40.8      | 2.12              | 52,800 |
| Amyl                                   |           |           | 4.34      | 8.66      | 32.0      | 2.00              | 53,000 |
| Hexyl                                  |           |           | 3.77      | 7.13      | 23.53     | 1.89              | 48,600 |
| Benzyl                                 |           |           | 1.54      | 3.70      | 16.24     | 2.40              | 62,500 |
| Isopropyl                              | 13.65     | 45.76     | 68.6      |           |           |                   | 38,700 |
| Sec.-butyl                             | 8.55      | 30.89     | 47.31     | 88.30     |           | 1.87              | 42,800 |
| Sec.-amyl                              |           |           | 34.70     | 68.02     |           | 1.96              | 51,800 |
| Sec.-hexyl                             |           | 13.53     | 25.96     | 47.38     |           | 1.82              | 47,500 |
| Benzene                                |           |           | 23.73     | 37.89     | 72.04     | 1.60              | 29,300 |

acid. Hemilian's process consisted in refluxing together the alkyl halide with an aqueous solution of ammonium sulfite, the reaction taking place according to the equation



This method was chosen because of the ease of manipulation and on account of the quantities desired. It had been employed by many workers but Hemilian was the only one who reported any yields. He claimed a 90% yield for the above case but this yield was never realized in this work. Also, due to the lower cost and greater ease of handling, the bromides were used in most cases above ethyl. This method, however, failed in the case of *sec.*-amyl, *n*-hexyl, *sec.*-hexyl and benzene sulfonic acids. In order to prepare the first three of these, the bromide was converted to the mercaptan, which was then oxidized by nitric acid to the corresponding sulfonic acid. The benzene sulfonic acid, free of the di-sulfonic acid, was prepared

TABLE II  
BOILING POINTS OF INTERMEDIATES USED IN PREPARATION OF SULFONIC ACIDS

| Alcohols   | B. p. (760 mm.), °C. | Halides            | B. p. (760 mm.), °C. |
|------------|----------------------|--------------------|----------------------|
|            |                      | Methyl iodide      | 42.4-42.8            |
|            |                      | Ethyl iodide       | 72.0-72.4            |
| Propyl     | 97.0-98.0            | Propyl bromide     | 70.9-71.2            |
| Isopropyl  | .....                | Isopropyl bromide  | 59.4-59.8            |
| Butyl      | 117.2-117.6          | Butyl bromide      | 101.2-101.5          |
| Sec.-butyl | 99.0-100.0           | Sec.-butyl bromide | 91.0-91.5            |
| Amyl       | 137.8                | Amyl bromide       | 129.6-129.8          |
| Sec.-amyl  | 119.3-119.6          | Sec.-amyl bromide  | 118.6-118.9          |
| Hexyl      | 100.5-101.0 (90 mm.) | Hexyl bromide      | 87.8-88.2 (90 mm.)   |
| Sec.-hexyl | 137.8-139.3          | Sec.-hexyl bromide | 143.6-144.1          |
|            |                      | Benzyl chloride    | 179.2-179.6          |

by hydrolysis of the acid chloride which had been cut on a precision still. Table II gives the constants of the intermediates used in these preparations.

**The Preparation.**—Hemilian's procedure was used for the preparation of the majority of the sulfonic acids, the exceptions being *n*-hexyl, *sec*.-amyl, *sec*.-hexyl, and benzene sulfonic acids. The first three of these were made by converting the bromide to the mercaptan and oxidizing the latter by concentrated nitric acid to the sulfonic acid. The acid solution was then evaporated to a negative test for nitrates, when it was neutralized by barium carbonate and evaporated to crystallization. In the case of benzene sulfonic acid, the acid chloride was hydrolyzed to the free acid, which in turn was converted to the barium salt by barium carbonate. The salts prepared by the Hemilian process were likewise converted to the barium salt for purification. The ammonium salts secured by this process were never isolated. The solutions, in some cases, were converted to the barium salt by boiling with an excess of barium hydroxide until free of ammonia, when the excess barium was precipitated by a stream of carbon dioxide; in other cases, litharge was used to remove the ammonia, the lead precipitated by hydrogen sulfide and the free acid thus obtained neutralized by barium carbonate. The barium salts were then purified by recrystallization from water and extraction by hot alcohol. The purity was calculated on the barium content found on precipitation as barium sulfate and was in all cases better than 99.5% as shown in Table III, which also gives the approximate yields of the barium salts obtained, calculated from the halides used.

TABLE III  
BARIUM ALKYL SULFONATES

| Ba salt of                  | Yield, % | Barium analysis, % |                     |       | Av. |
|-----------------------------|----------|--------------------|---------------------|-------|-----|
|                             |          | Calcd.             | Found               |       |     |
| Methyl sulfonic             | 56.5     | 41.94              | 42.06, 42.03, 42.02 | 42.04 |     |
| Ethyl sulfonic              | 62.0     | 38.63              | 38.58, 38.60        | 38.59 |     |
| Propyl sulfonic             | 50.0     | 35.81              | 35.83, 35.81        | 35.82 |     |
| Isopropyl sulfonic          | 52.0     | 35.81              | 35.63, 35.63        | 35.63 |     |
| Butyl sulfonic              | 60.0     | 33.37              | 33.34, 33.34        | 33.34 |     |
| <i>Sec.</i> -butyl sulfonic | 50.0     | 33.37              | 33.24, 33.30        | 33.27 |     |
| Amyl sulfonic               | 70.0     | 31.24              | 31.17, 31.27        | 31.22 |     |
| <i>Sec.</i> -amyl sulfonic  | 50.0     | 31.24              | 31.22, 31.17        | 31.20 |     |
| Hexyl sulfonic              | 62.0     | 29.37              | 29.37, 29.36        | 29.37 |     |
| <i>Sec.</i> -hexyl sulfonic | 52.0     | 29.37              | 29.37, 29.37        | 29.37 |     |
| Benzene sulfonic            | ..       | 30.42              | 30.34, 30.38        | 30.36 |     |
| Benzyl sulfonic             | 50.0     | 28.64              | 28.56, 28.54        | 28.55 |     |

**The Decomposition.**—Preliminary test runs showed the barium salts were not all sufficiently soluble to obtain solutions of the desired concentrations so conversion to the sodium salts was found necessary. This was accomplished by addition of sodium carbonate to solutions of the



barium salts. The solutions of the sodium salts so obtained were analyzed by evaporation of a sample to dryness, ashing to sodium sulfate and correcting this value for the slight excess of sodium carbonate present by titration of a second sample with standard acid. Approximately molal solutions of all the acids were prepared in this way.

In carrying out the reaction, 5 cc. of solution mixed with 5 cc. of approximately 4 *N* sodium hydroxide was heated in a steel bomb for three hours to temperatures ranging from 315 to 375°. The products of the reaction were then washed from the bomb into excess acidified standard iodine solution and the excess back titrated by standard thiosulfate solution. This gave the values called percentage splitting on the sulfite basis. The possibility of sulfate splitting was checked by precipitation of the sulfate from the oxidized solution. This value always ran slightly higher than that on the sulfite basis but not sufficiently so to be of any consequence. Table IV gives a summary of the values found in the decompositions.

TABLE IV  
ALKALINE DECOMPOSITION OF ALIPHATIC SULFONIC ACIDS

The bomb solution was made up of 5.0 cc. of the sodium sulfonate solutions of the specified concentrations and 5.0 cc. of 3.70 *N* sodium hydroxide solution. The period of heating was three hours. Where several runs were made at the same temperature, the average is given in the last column.

| Sulfonate | Concn.,<br>moles/liter | Temp., °C. | % Splitting, sulfite basis   | • Av. |
|-----------|------------------------|------------|------------------------------|-------|
| Methyl    | 1.031                  | 345        | 1.5                          |       |
|           |                        | 355        | 2.8                          |       |
|           |                        | 375        | 11.0                         |       |
| Ethyl     | 1.016                  | 315        | 18.8                         |       |
|           |                        | 335        | 45.1                         |       |
|           |                        | 345        | 62.7                         |       |
|           |                        | 355        | 73.7, 74.0                   | 73.8  |
| Propyl    | 0.9800                 | 345        | 20.2                         |       |
|           |                        | 355        | 36.0                         |       |
|           |                        | 375        | 71.1, 73.4, 73.3             | 72.6  |
| Butyl     | 0.9401                 | 345        | 17.3                         |       |
|           |                        | 355        | 32.1, 31.6                   | 31.8  |
|           |                        | 375        | 71.2, 69.7, 70.4, 64.5, 65.1 | 68.2  |
| Amyl      | 1.008                  | 345        | 13.3                         |       |
|           |                        | 355        | 24.0, 24.7                   | 24.3  |
|           |                        | 375        | 61.8, 61.6                   | 61.7  |
| Hexyl     | 1.061                  | 345        | 11.7                         |       |
|           |                        | 355        | 20.7                         |       |
|           |                        | 375        | 51.7, 51.2                   | 51.5  |
| Benzyl    | 1.014                  | 345        | 5.0                          |       |
|           |                        | 355        | 11.5                         |       |
|           |                        | 375        | 40.2, 40.0                   | 40.1  |
| Isopropyl | 0.9975                 | 315        | 35.0                         |       |
|           |                        | 335        | 73.6                         |       |
|           |                        | 345        | 88.6                         |       |

TABLE IV (Concluded)

| Sulfonate          | Concn.,<br>moles/liter | Temp.,<br>°C. | % Splitting,<br>sulfite basis | Av.  |
|--------------------|------------------------|---------------|-------------------------------|------|
| <i>Sec.</i> -butyl | 0.9226                 | 315           | 24.1                          |      |
|                    |                        | 335           | 60.8                          |      |
|                    |                        | 345           | 75.2                          |      |
|                    |                        | 355           | 91.3, 91.8                    | 91.5 |
| <i>Sec.</i> -amyl  | 1.145                  | 345           | 64.2, 64.2                    | 64.2 |
|                    |                        | 355           | 84.8                          |      |
| <i>Sec.</i> -hexyl | 1.015                  | 335           | 35.0                          |      |
|                    |                        | 345           | 54.2, 55.6                    | 54.9 |
|                    |                        | 355           | 75.0                          |      |
| Benzene            | 0.9876                 | 345           | 5.0                           |      |
|                    |                        | 355           | 11.5                          |      |
|                    |                        | 375           | 40.0, 40.2                    | 40.1 |

### Summary

1. A series of aliphatic sulfonic acids has been prepared.
2. The decomposition of the sodium salts of these acids in alkaline solution at high temperatures and pressures has been determined.
3. The order of the reaction has been determined and the course of the reaction indicated.
4. The velocity constants and heats of activation have been calculated.

## BIOGRAPHY

Frederick Carver Wagner was born in Hanover, Pennsylvania, November 27, 1899. He received his early education in the public schools and was graduated from the Hanover High School in 1917. The years 1917-21 were spent at Dickinson College from which he received the A.B. degree, and 1921-24 at the Massachusetts Institute of Technology from which he received the B.S. degree.

He was employed from 1924-26 in the Jackson Laboratories of the Du Pont Dye Works; during 1926 by the Commercial Solvents Corporation and again during 1927 in the Jackson Laboratories.

The years 1927-29 were spent as a graduate student in the Department of Chemistry at the Johns Hopkins University during which time he also served as student assistant in Organic Chemistry.







